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Editorial

Photopolymerisation chemistry

During the last 30 years or so, the fields of photopolymerisation and photoimaging science and technology have grown from subjects of esoteric research specialities into major industrial developments. They are now fields of central importance in polymer science and technology. Inherent in these technologies, is the use of a photoactivator system which is capable of absorbing the incident UV and/or visible radiation wavelengths used for converting a monomer or prepolymer system into a crosslinked network. In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiator molecules. These have been designed to have desirable properties such as higher activity or greater speed coupled with lower migration rates and/or water solubility. Two areas of importance in this regard are the development of monomeric and polymeric photoinitiators with reactive functionalities while cationics have also begun a revitalisation program. These are all capable of co-reaction with the monomer or prepolymer system in some way. In addition, one can extend their absorption spectrum, thus imparting greater spectral sensitivity to the visible region of the spectrum. The last point is now of some importance, particularly for laser-induced polymerisations and holography. This special issue draws together a number of key workers in this important field to highlight areas of their specialisations and to provide the reader with a flavour of what is happening today.

Many of the articles here deal with developments in novel cationics. Crivello and Jang provide an insight into some new anthracene onium salts with 9,10-dialkoxyanthracenes providing high photoactivity as photosensitisers vinyl ether and epoxy monomers. On the other hand, Sipani and Scranton have investigated kinetics of the cationic photopolymerisation of phenyl glycidyl ether with two types of iodonium salts. Although under illumination the kinetics are similar, one of the salts (borate type) exhibits a different reactivity in the dark with a higher limiting conversion. Anthracene bound sulphonium salts are also investigated by the Pappas group where silver salts can be avoided. As well as novel synthetic methodologies being provided here evidence is also provided for electron transfer from the anthracene chromophore to the sulphonium salt. Phenacyl onium salts are shown by the Yagci group to exhibit both free radical and zwitterionic activities, the latter also occurring via an electron transfer step. They are claimed to be very useful for curing conventional multifunctional monomers. Complexes of iron have been investigated by Neumann's group where interestingly they find that methanol complexes are more effective than those directly utilising a monomer such as MMA. Different complexes also exhibit different mechanisms. Bowmans group have predicted useful models for multivinyl free radical polymerisations taking into account various controlling parameters in each case such as diffusion control, termination steps, chain length and chain transfer steps. Each process and its influence of the kinetics and rate are carefully analysed giving a useful picture of the more important controlling factors. An original approach and model has also been developed by Fouassier's group for laser-induced photoacoustic calorimetry. Here cleavage processes are modelled and compared with photodissociation enthalpies. Sulphur containing initiators are probed by Paczkowski's group for free radical photopolymerisation of vinyl monomers. Useful outcomes and mechanistic processes are presented for a variety of systems developed in recent years by this group. Lastly, the CSIC group of Catalina have made significant in-roads in recent years into polymeric photoinitiators. These are reviewed and compared with model monomeric initiator systems with a number having some significant advantages of commercial significance combining both high activity with non-migration.

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